

Element-specific photo-breakdown studies of environment-relevant molecules in the VUV to soft X-ray region at Beamline 6.3.2 and Beamline 9.3.1

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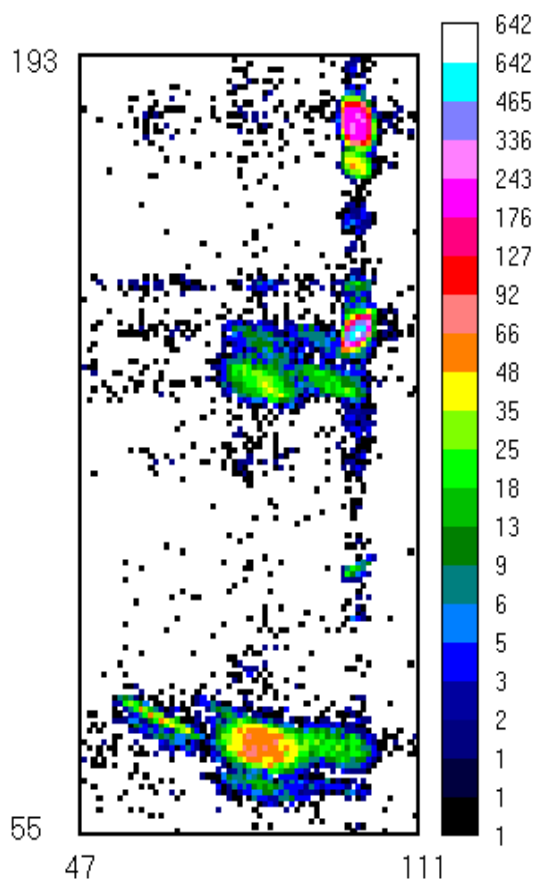
The large-scale industrial consumption of chlorofluorocarbons (CFCs) has attracted a lot of attention due to their destructive effects on atmospheric ozone and global change. Since the Montreal Protocol¹ a decade ago, there is now a serious effort made by many industries to replace their traditional CFC-based products (involving the so-called Annex A and B controlled substances), including refrigerants, aerosol propellants, plasma etchants, etc., with the more environment-friendly substitutes, which consist primarily of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and their derivatives. Many of the photochemical properties and electronic structures of these replacement molecules are, however, not known, which creates an unsettling potentiality that heavy commercial usage of these replacement molecules may in turn generate unforeseen adverse effects on the environment. Recently, we have begun a systematic study to examine the photoexcitation of a series of common substitutes, including HCFCs² and HFCs. In particular, a comprehensive data base of precise photoabsorption and photofragmentation cross sections (and branching ratios) of these industrially relevant molecules is being determined in the VUV to soft-X-ray region by using time-of-flight and photoion double or triple coincidence techniques.³ The characteristic photoion-photoion coincidence (PIPICO) spectra not only give a detailed picture of the dissociation dynamics following photoexcitation,^{4,5,6} but also provide an element-specific fingerprint of the target of interest if the excitation photon energy is tuned to specific ionization edges. This type of photodissociation information may be used ultimately for diagnostic purposes of unknown waste emission and for other smog analysis.

In addition to the obvious practical relevance, the measurements of photoabsorption and photofragmentation cross sections of HCFCs and HFCs can be used to provide important insight to shape resonance phenomena and non-Franck-Condon behaviour^{7,8} and to critically evaluate modern photoionization theories and electronic structure calculations. In particular, the presence of resonances (usually manifested as broad, intense features) in the photoabsorption and photoionization cross section profiles of small molecules has already attracted a lot of recent attention.^{4,7} The interplay between shape resonances (a resonant transition to a quasibound state that couples to the continuum) and autoionizing resonances (a multielectron discrete transition to an excited state that decays by ejection of one or more electrons) is believed to play a key role in molecular photoionization dynamics. The CF_nCl_{4-n} (n=0-4) and HCF_mCl_{3-m} (m=0-3) series provide an interesting variety of benchmark systems for investigating the geometry effect on the nature of the observed shape resonances. The devolution of molecular symmetry from CF_nCl_{4-n} (n=0-4) to its monohydride homologs, HCF_mCl_{3-m} (m=0-3), would clearly reduce the hypothesized “centrifugal potential barrier” that leads to the shape resonance effect. The increasing chlorination in these two series may also produce interesting effects due to expansion of the diffuse bonding region (and the size of the molecule). Furthermore, atom-specific effects involving different “localized” inner shells [e.g., C-K, F-K, and Cl-L shells of CF_nCl_{4-n} (n=0-4)⁹ and HCF_mCl_{3-m} (m=0-3)]¹⁰ would be of particular interest to differentiate contributions from the so-

called inner-well and outer-well states in the observed resonance features. The cage and partial-cage structures of these molecules represent model systems to investigate the fine-structure phenomena near the absorption edge (XANES) as well as diffraction-related effects (such as EXAFS). Moreover, the studies of photofragmentation cross section profiles will further elucidate the interplay between electronic structure and geometry in cation chemistry and spectroscopy. Of particular interest is the change in the electronic structure of the cation and the subsequent breakup dynamics as a result of photoexcitation at different sub-shells localized at specific sites of the molecule. Finally, although most of the photochemical atmospheric processes were found to occur below 5 eV, these valence and inner shell studies offer new information about the excited (final) states, which are important to quantum mechanical modelling of the potential curves involved in the photodissociation dynamics of these atmospheric processes.

The significantly improved brightness available at the Advanced Light Source makes it possible to determine the photoabsorption and photofragmentation cross sections in these large molecular systems with unprecedented resolution, precision and speed. The markedly improved signal-to-noise also makes viable the previously challenging experiments involving low signal rates (e.g., the non-dipole states) and coincidence detection. In a series of photodissociation studies on the common CFC and HCFC series at different ionization edges of Cl, F and C by using photon-triggered PIPICO techniques at Beamline 6.3.2 and Beamline 9.3.1, we have demonstrated the unprecedented timing (energy) resolution achievable at the ALS, which allowed us to resolve and identify, for the first time, many of the photofragments resulting from photodissociation of these large, complex molecules. Other photofragmentation and photoabsorption experiments of the so-called Annex-C controlled substances (in particular, fluoroethanes)¹ also demonstrate the enormous potential of using the PIPICO spectra for element-specific

chemical analysis and for probing changes in the photo-breakdown behaviour across different ionization edges. The wavelength tunability of the synchrotron beamlines (appropriate for different inner-shell ionization edges) offers a powerful means to investigate near-resonance effects localized at specific elements (Cl, F, or C) in the photo-breakdown process. In-situ formation of some rather unexpected (short-lived) species from the photofragments has been observed. The presence of these exotic species suggests the viability of using these core-specific techniques as a means to study ultra-fast photo-induced radical and gas-phase ion chemistry. Finally, the intense



A typical charge separation spectrum of selected ions produced during double photoionization of Freon 22 (HCF_2Cl) at a Cl 2p resonance. Data collected at Beamline 6.3.2.

brightness deliverable at the interaction region offers an unique opportunity to investigate “new” decay processes resulting from not just the dications, but also for the first time triply and other multiply charged photoions by using triple and multiple photoion coincidence techniques. Together these experiments at the ALS offer the first comprehensive research program on the photodissociation phenomena of complex molecular systems (of technological interest) over a wide energy range from the VUV to soft X-ray region and are expected to have a wide impact on areas such as environmental research, radiation and space sciences, fusion, lasers, aeronomy and astrophysics.

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- ⁹ T.N. Olney, N.M. Cann, G. Cooper, C.E. Brion, *Chem. Phys.* **223**, 59 (1997), and refs. therein.
- ¹⁰ In contrast to the considerable amount of energy and cross section data on the photoabsorption and photoionization processes of CF₄ [T.A. Carlson et al., *J. Chem. Phys.* **81**, 3828 (1984)], CF₃Cl, CF₂Cl₂, CFC₃ and CCl₄ (Ref. 9), there is limited information on their more environment-friendly “temporary” substitutes, HCF₃, HCF₂Cl, HCFC₂, and HCCl₃, and other HCFC and HFC derivatives (which are now becoming more readily available in the marketplace). See Ref. 2 for a review of the previous work.

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